Methyl 9(10)-Carboxystearate by Catalytic Oxidation of Hydroformylated Oleate[1]

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ABSTRACT

Methyl 9(10)-formylstearate from hydroformylated oleate is autoxidized effectively to the corresponding carboxystearate in the presence of metal naphthenates at 20 C. Up to 95% conversion is obtained by treatment with Ca naphthenate for 24 hr. Catalyst activity based on disappearance of formylstearate approximates the following order: Co>Pb>Mn>Ce>Fe>Zr>Ca. Decreasing yields of carboxyester obtained with different catalysts follow the approximate order: Ca>Pb≈Fe≈Zr≈Mn>Co>Ce. The active redox metal catalysts such as Co, Ce and Mn produce varying amounts of methyl stearate, epoxy-, keto- and hydroxystearate as side products. Ca naphthenate minimizes free radical decarbonylation and other side reactions. Mechanisms are proposed for the formation of side products.

INTRODUCTION

Recently a Rh catalyst has been discovered to be highly selective for the hydroformylation of oleic esters into 9(10)-formylstearic derivatives (1). Oxidation of the formyl group yields esters with a branched carboxy acid that may be commercially useful derivatives in the preparation of lubricants, plasticizers, polyamides and polyesters.

Autoxidation of aldehydes is accelerated by metal catalysts in several commercial processes. Acetic acid is produced by the oxidation of acetaldehyde catalyzed by metal salts. Manganese acetate is generally considered the best for acetic acid production and a mixture of cobalt and copper salts is used for the preparation of acetic anhydride (2). Acetic acid is formed through the acetaldehyde monoperacetate intermediate which is catalytically decomposed by metal ions. Manganese and cobalt acetate catalyze not only peracetic acid decomposition but also the peracetic acid reaction with acetaldehyde (3).

This paper presents studies on the metal-catalyzed autoxidation of methyl 9(10)-formylstearate for the preparation of the corresponding methyl carboxystearate. Results of chemical oxidations with permanganate, dichromate and hydrogen peroxide are included for comparison.

RESULTS

Formation of methyl 9(10)-carboxystearate by catalytic autoxidation of methyl 9(10)-formylstearate was followed by gas liquid chromatography (GLC) and titration analyses. Analyses of products from catalytic autoxidations are summarized in Table I. GLC showed unreacted formyl as well as byproduct formation whereas acid value measured only carboxystearate. Experimental error in titration may account for some of the discrepancies between GLC and acid values. The highest yield of methyl 9(10)-carboxystearate in 24 hr was produced in the Ca-catalyzed reaction. Approximately 9% of unreacted formyl ester remained in the uncatalyzed reaction compared to 3.8% in the Ca autoxidation. After 48 hr, only trace amounts of formyl ester were left in the Ca autoxidation. More rapid disappearance of formylstearate was obtained with Co, Mn, Ce and Pb but these autoxidations were accompanied by the formation in larger amounts of other products including methyl stearate, epoxy-, keto- and hydroxystearate. Other

TABLE I

Catalytic Autoxidation of Methyl 9(10)-Formylstearate[a]

		Composition (GLC), %					
Catalyst, 0.5%	Time, hr	Carboxy-stearate	Formyl-stearate	Stearate + oleate	Keto + hydroxy-stearate	Other[b]	Acid value, % carboxystearate
Control[c]	8	71.7	17.5	5.4	4.7	0.7	69.8
	24	87.2	8.9	2.2	1.3	0.4	77.6
Ca[c]	8	75.8	10.5	4.4	3.6	5.7	86.5
	24	91.6	3.8	3.8	0.7	0.1	87.2
Pb	2	61.9	26.7	6.0	3.8	1.3	61.1
	4	76.9	6.0	6.2	8.6	2.3	76.7
	24	79.9	2.6	5.6	10.0	1.1	81.2
Fe	2	48.6	34.8	8.8	4.3	1.3	54.6
	4	65.7	20.0	6.2	5.2	2.3	63.0
	24	79.9	2.6	5.6	10.0	1.3	77.4
Zr	2	43.1	44.6	8.5	3.1	0.7	61.0
	4	57.5	25.8	8.3	5.5	2.9	67.0
	24	76.0	8.1	2.7	6.3	6.9	75.1
Mn	2	32.7	55.4	6.1	2.5	3.3	67.3
	4	74.3	7.4	10.5	5.9	1.9	---
	24	79.4	None	9.5	9.3	0.8	70.5
Co[c]	24	65.3	None	18.9	14.4	1.4	63.4
Ce	2	35.6	39.6	15.4	7.7	0.7	39.6
	4	52.3	14.8	19.4	13.1	0.4	---
	24	58.1	1.0	17.2	23.7	None	58.1

[a] Starting material: 92.5% formylstearate, 4.0% carboxystearate and 3.5% stearate + oleate.
[b] Includes: epoxystearate, diformylstearate, other unidentified material.
[c] See rates in Figure 1.

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[2] No. Market. Nutr. Res. Div., ARS, USDA.

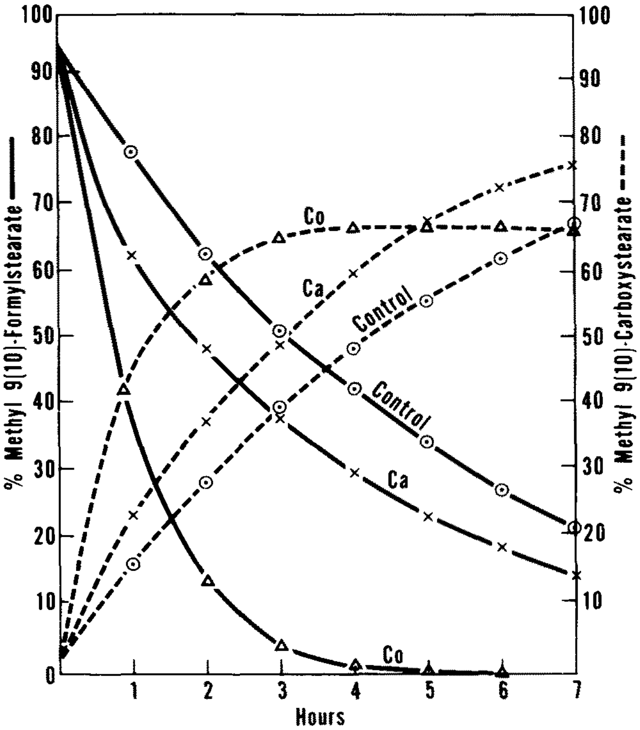


FIG. 1. Effect of Ca and Co catalysts on disappearance of formylester and on formation of carboxyester at 20 C. Dotted curves–rate of formation of carboxystearate. Solid curves–rate of disappearance of formylstearate.

effective catalysts for carboxyester formation included Pb, Zr and Fe.

Figure 1 shows rate curves for disappearance of formylstearate and formation of carboxystearate with Ca and Co compared to the control sample. Rate curves for the formation of carboxystearate with Pb, Ce and Mn were similar to that of Co. Autoxidation curves for Fe and Zr resembled more closely that of Ca. If catalyst activity is based on disappearance of formylstearate after 4 hr oxidation the following order can be approximated: Co> Pb>Mn>Ce>Fe>Zr>Ca. Based on yield of carboxyester at 24 hr the approximate order is: Ca>Pb≈Fe≈Zr≈Mn> Co>Ce.

In Figure 2, products of Co- and Ca-catalyzed autoxidations are compared with the starting material. Identified products (GLC peaks) included: methyl oleate (A), stearate (B), epoxystearate (C), 9(10)-ketostearate (D), 9(10)-hydroxystearate (E), 9(10)-formylstearate (starting material) (F) and 9(10)-carboxystearate (G). Isolated products were purified by column chromatography, preparative GLC or crystallization. Identification was based on chemical analyses, melting points, mass spectrometry, IR and comparison of GLC and thin layer chromatography (TLC) retention times of authentic materials.

To determine whether methyl oleate is a byproduct, high-purity methyl 9(10)-formylstearate was autoxidized at 20 C. With 0.5% Co naphthenate, 1.2% methyl oleate was detected in the oxidation product together with methyl stearate, keto-, hydroxy- and a trace of epoxystearate. However, the Ce-catalyzed and control autoxidations gave only methyl stearate, keto- and hydroxystearate.

To aid in elucidating the mechanism of byproduct formation, peroxide values were determined during catalytic autoxidations. Figure 3 shows that with Co and Ce an initial rapid increase in peroxide occurs followed by a decrease after the first 30 min. Peroxide development in the Ca-catalyzed autoxidation is negligible and significantly smaller than the control. Ca exhibits, therefore, an inhibiting effect in the development of peroxide during autoxidation of formylstearate.

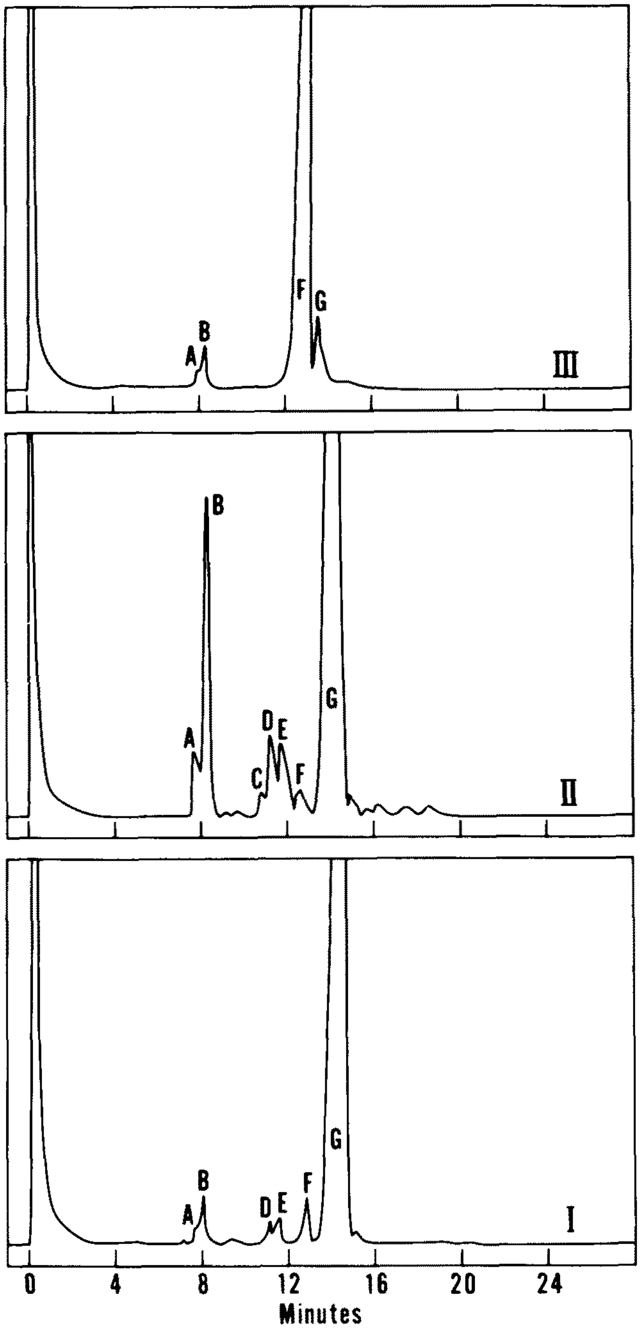


FIG. 2. Gas chromatogram of (I) product from Ca naphthenate oxidation, (II) product from Co naphthenate oxidation and (III) methyl 9(10)-formylstearate starting material. (A) Methyl oleate, (B) methyl stearate, (C) methyl epoxystearate, (D) methyl 9(10)-ketostearate, (E) methyl 9(10)-hydroxystearate, (F) methyl 9(10)-formylstearate and (G) methyl 9(10)-carboxystearate.

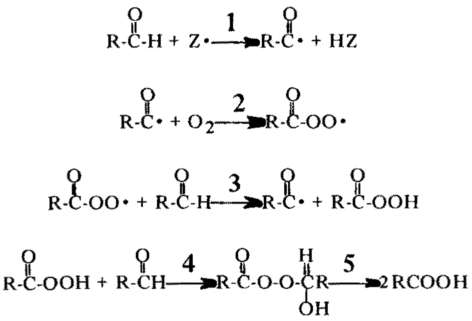
A few experiments were carried out with binary mixtures of metal catalysts to determine whether autoxidation could be accelerated with a minimum of side reactions. However, mixtures of Ca + Co and Ca + Fe produced considerable byproduct.

Permanganate, dichromate and alkaline hydrogen peroxide have been included in this study for comparative purposes. Oxidation of methyl 9(10)-formylstearate with permanganate and dichromate yielded 96.1 and 98.2% carboxystearate, respectively. Oxidation with alkaline hydrogen peroxide produced 27% carboxystearate and approximately equal amounts of keto- and hydroxystearate (31.2 and 32.2%, respectively). Alkaline hydrogen peroxide oxidation appears to follow a typical Baeyer-Villiger reaction (4) yielding products formed by an ionic mechanism. These byproducts are also formed by the free radical catalysts such as Co, Ce and Mn salts. Permanganate and dichromate oxidations of formylstearate have been satisfactorily used on a small scale. On a larger scale, however, problems in isolating the product have been experienced.

DISCUSSION

A free-radical chain mechanism is generally accepted for the autoxidation of aldehydes (2,3,5). Free-radical chain initiation may involve traces of dissolved peroxide, metal ion catalysts undergoing a change in oxidation state, photolytic or thermal cleavage (6). In the autoxidation of benzaldehyde catalyzed by cobalt acetate, a direct reaction has been established between the aldehyde and the metal catalyst in its higher valency state (7).

The free-radical, metal-catalyzed autoxidation of methyl 9(10)-formylstearate to methyl 9(10)-carboxystearate may be considered to proceed, as in other aldehydes (3,6), by the following initiation (reaction 1), propagation (reactions 2 and 3) and termination (reactions 4 and 5) steps:



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + Z\bullet \xrightarrow{1} R\text{-}\overset{O}{\overset{\|}{C}}\bullet + HZ$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\bullet + O_2 \xrightarrow{2} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OO\bullet$$

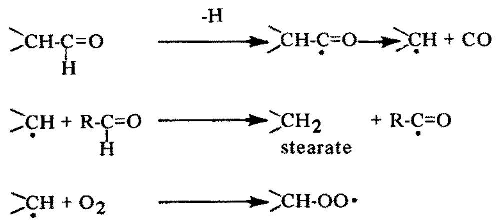
$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OO\bullet + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \xrightarrow{3} R\text{-}\overset{O}{\overset{\|}{C}}\bullet + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OOH$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OOH + R\text{-}\overset{O}{\overset{\|}{C}}H \xrightarrow{4} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\underset{OH}{\overset{H}{C}}R \xrightarrow{5} 2RCOOH$$

Steps 4 and 5 do not involve free radicals and may be regarded as the Baeyer-Villiger pathway. Metal ions accelerate autoxidation of aldehydes (6) by catalyzing decomposition of the peracid intermediate (reaction 3) and the peracid reaction with the aldehyde (reaction 4). Although various metal complexes have been invoked in these reactions, the exact species involved are not known.

Decarbonylation is an important side reaction observed during catalytic autoxidation of various aldehydes. Thuring and Peret (8) found that 2-ethylhexanal and 4-methylpentanal are easily decarbonylated in the presence of soluble salts of Ni, Co and Mn. This reaction is accompanied by the formation of saturated ketones and is negligible in normal aldehydes. Decarbonylation occurs by homolytic decomposition of aldehydes (9) and involves an acyl radical, $R\underset{\bullet}{C}=O$, derived by hydrogen abstraction. The acyl radical formed during acrolein oxidation is coordinated with the metal catalysts and plays a key role in the decarbonylation (10). Ladhabhoy and Sharma (11) reported that the oxidation of 2-ethylhexaldehyde catalyzed by manganese acetate is accompanied by the formation of *n*-heptane, 3-heptanone and 3-heptanol. Decarbonylation was limited by maintaining temperature below 30 C.

Decarbonylation of methyl 9(10)-formylstearate during autoxidation catalyzed by the active redox metal catalysts would account for the formation of methyl stearate, keto- and hydroxystearate. These byproducts may be formed according to the following reactions:



$$>CH\text{-}\underset{H}{\underset{|}{C}}=O \xrightarrow{-H} >CH\text{-}\underset{\bullet}{C}=O \longrightarrow >\underset{\bullet}{C}H + CO$$

$$>\underset{\bullet}{C}H + R\text{-}\underset{H}{\underset{|}{C}}=O \longrightarrow \underset{\text{stearate}}{>CH_2} + R\text{-}\underset{\bullet}{C}=O$$

$$>\underset{\bullet}{C}H + O_2 \longrightarrow >CH\text{-}OO\bullet$$

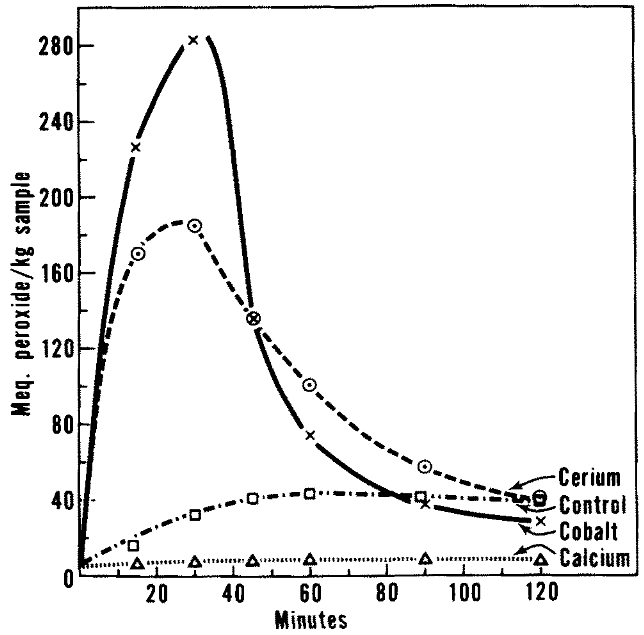


FIG. 3. Peroxide development during Co, Ce and Ca autoxidations of formylester at 20 C.

$$2 >CH\text{-}OO\bullet \longrightarrow \underset{\text{keto-}}{>C=O} + \underset{\text{hydroxy-}}{>CHOH} + O_2$$

stearate

Ketostearate may also result from the oxidation of hydroxystearate.

Methyl oleate in the Co-catalyzed autoxidation of high-purity methyl 9(10)-formylstearate may be formed by disproportionation of the type:

$$\text{-}\underset{\bullet}{\overset{H}{C}}\text{-}CH_2\text{-} + \text{-}\underset{\bullet}{\overset{H}{C}}\text{-}CH_2\text{-} \longrightarrow \text{-}CH_2\text{-}CH_2\text{-} + \text{-}CH=CH\text{-}$$

This disproportionation apparently does not occur with Ce or in the uncatalyzed reaction. Alternatively, oleate may be formed by decarbonylation accompanied by dehydrogenation.

Epoxystearate may arise from either a peroxy radical undergoing allylic hydrogen abstraction or by epoxidation of methyl oleate with peracid formed during the reaction.

In this study Ca naphthenate was shown to be a unique catalyst for the efficient conversion of formylstearate to carboxystearate. It does not promote free-radical formation as evidenced by the very small accumulation of peroxide during autoxidation. In fact, the results in Figure 3 indicate an inhibiting effect of Ca on the development of peroxide. The effectiveness of Ca naphthenate may be explained by formation of a stable chelate with the aldehyde group which does not undergo hydrogen abstraction. Further reaction with oxygen would lead to the formation of a carboxy acid Ca chelate apparently by a nonradical mechanism not involving a titratable peroxy group. The resulting chelate is then dissociated to product without degradation. The more active redox catalysts such as Co, Ce and Mn would form less stable chelates with the aldehyde and carboxy acid groups which catalyze free-radical decarbonylation, peracid decomposition and the peracid-aldehyde reaction (3,6). A more detailed picture of the mechanism cannot be made until the corresponding metal coordination complex intermediates with aldehyde and carboxy acid products are further elucidated.

EXPERIMENTAL PROCEDURES

Materials and Analyses

Methyl 9(10)-formylstearate was prepared as described previously (1). Purity determined by GLC exceeded 90%. Impurities included 2-5% oleate + stearate, 1-4% carboxystearate and 1-2% diformylstearate. High-purity (99.5%) methyl 9(10)-formylstearate was prepared by fractional distillation (bp 158-159 C at 0.050 mm Hg). The only detectable impurity was 0.5% stearate. Metal naphthenates were obtained from Tenneco Chemicals, Inc. and the Zr catalyst (Advacar Zirco Drier) from Advance Solvent and Chemical Co.

Samples (ca. 1 mg) were methylated with diazomethane and analyzed by GLC programmed at 170-300 C, 4 C/min, at a flow rate of 30 cc/min on an F&M instrument Model 5750 equipped with a 6 ft x 1/4 in., 3% JXR column. Peroxide and acid values were determined by the Official AOCS Method (12). Samples were isolated by column chromatography and preparative GLC and identified by mass spectrometry, IR, microanalysis and TLC (13). For preparative GLC, samples were collected in a 2 in. No. 14 Teflon tube inserted at the exit port of the instrument. Several collections were made and recycled to increase purity.

Small Scale Catalytic Autoxidations

Methyl 9(10)-formylstearate (25 g) and the metal catalyst (0.5% based on weight of formyl ester) were charged into a 100 ml graduated cylinder immersed in a 20 C (±1 C) water bath. Air measured by a Wet Test Meter (flow rate: 20 liters/min) was dried through Drierite and then introduced into the reaction mixture through a fritted glass sparger tube. Control runs were made under the same conditions without catalyst. Samples were analyzed periodically by GLC, neutral equivalent and peroxide values.

Large Scale Ca Naphthenate Autoxidation

Methyl 9(10)-formylstearate (500 g, 92%) and Ca naphthenate (50 ml, 5% Ca) were placed in a 2000 ml graduated cylinder equipped with a flat fritted glass ebulator (5.5 cm diam) and an external cooling coil and bath to maintain the temperature at 20 C. A constriction at the 1500 ml mark held a small inverted funnel to control excessive splashing and to hold the ebulator tube in position. Compressed air (18-20 liters/min) was passed through a column of Drierite and then through the reaction mixture for 24 hr. Crude yield was 560 g. Analysis by GLC showed 84.1% methyl carboxystearate, 3.6% oleate + stearate, 3.6% hydroxy- + ketostearate and 4.9% formylstearate.

Purification

A portion of crude autoxidized product (196 g) was treated with urea (100 g) and methanol (200 ml) to remove straight chain impurities. After recrystallization of the urea adduct the methanol solutions were combined, poured into water and extracted with ether. The ether solution was washed with water, stripped to dryness and the product recrystallized from *n*-hexane (300 ml) at -20 C. After filtration 100 ml of *n*-hexane was removed and a second crop of crystals was obtained. The methyl 9(10)-carboxystearate obtained (135.3 g, 74% yield) was 99% pure. (Neutral equivalent: 345, calc., 342.)

Separation and Identification of Oxidation Byproducts

The urea adduct from the preparation of methyl carboxystearate above was decomposed with water and extracted with ether. After washing and drying and removing the ether, the byproducts (15 g) were dissolved in *n*-hexane and passed through two 10 g alumina columns. The first column retained most of the remaining methyl carboxystearate. The second column was eluted with methanol and methyl 9(10)-hydroxystearate was crystallized from the eluate. (Peak E, Fig. 2) (mp 42-43 C). Analysis: Calc. for $C_{19}H_{36}O_3$: C, 72.55; H, 12.17. Found: C, 73.19; H, 12.65.) Mass spectrometry showed prominent peaks at M - 18 = 296 and at M = 155, 158 and 187 for methyl 9-hydroxy- and at M = 169, 172 and 201 for methyl 10-hydroxystearate. IR analysis showed strong bands for hydroxyl (3.0 μ), carbonyl (5.75 μ) and methyl ester (8.05, 8.35 and 8.55 μ).

The hexane solution collected from the alumina column was passed through several 5 g silicic acid columns and eluted with methanol. After removal of the methanol the product was recrystallized from methanol and identified as methyl 9(10)-ketostearate (Peak D, Fig. 2) (mp 40-42 C. Analysis: Calc. for $C_{19}H_{36}O_3$: C, 73.02; H, 11.61. Found: C, 73.12; H, 11.96.) Mass spectrometry showed prominent peaks at M = 312 and at M = 170, 185 and 200 for the methyl 9-keto- and at M = 156, 199 and 214 for methyl 10-ketostearate. IR analysis showed strong bands for ester (5.75 μ), ketocarbonyl (5.83 μ) and for methyl ester (8.05, 8.35 and 8.55 μ).

After crystallization of the methyl ketostearate the methanol filtrate was evaporated to dryness and fractionally crystallized several times at -20 C from a smaller amount of methanol to give a product identified as epoxystearate (Peak C, Fig. 2). IR analysis showed strong absorption bands for epoxy (11.25 μ), carbonyl (5.75 μ) and methyl esters (8.05, 8.35 and 8.55 μ). Oxirane analysis gave 86.7% of the value calculated for methyl epoxystearate. A pure sample for analysis was obtained by preparative GLC. (Analysis: Calc. for $C_{19}H_{36}O_3$: C, 73.02; H, 11.61. Found: C, 73.55; H, 12.07.) Mass spectrometry showed prominent peaks at M = 312, M - 18 = 294, M - 31 = 281, M - 18 = 263, M - 18 - 32 = 261 and M - 157 = 155. The same peaks were obtained with an authentic sample of methyl 9(10)-epoxystearate.

The hexane solution from the silicic acid columns was stripped to dryness and the residue was recrystallized several times from methanol to give methyl stearate (Peak B, Fig. 2), mp 36-37 C. The major component remaining after the removal of the methyl stearate was methyl oleate (Peak A, Fig. 2) identified by GLC retention times on an EGSS-X column. Component B (Fig. 2) was also isolated by preparative GLC and identified by mass spectrometry. Methyl 9(10)-formylstearate (Peak F) was collected in the same way and characterized by TLC and GLC retention.

Chromate Oxidation

Methyl formylstearate (10.7 g) was dissolved in 150 ml glacial acetic acid and, while being rapidly stirred, a solution of potassium dichromate (10.0 g), sulfuric acid (5.5 ml), glacial acetic acid (10 ml) and 13 ml water was added. The reaction mixture was stirred vigorously and the temperature was maintained below 20 C for 1 hr. The mixture was then poured into cold water and extracted with ether. After washing with water until neutral the ether was distilled. (Yield: 10.8 g; neutral equivalent, 343.1; calc., 342; GLC analysis: methyl carboxystearate: 98%, stearate 2%.)

Permanganate Oxidation

Potassium permanganate (1.7 g) and sodium bicarbonate (1.6 g) were dissolved in water (50 ml) and added slowly to a stirred solution of methyl 9(10)-formylstearate (5 g) in acetone (100 ml). The temperature was maintained below 20 C for 2 hr. A filter paper test for MnO_4 was faintly positive. The mixture was acidified with hydrochloric acid and small amounts of sodium bisulfite were added to decolorize the manganese dioxide. The solution was diluted with water and extracted with ether. After washing, removing the ether and stripping the product to dryness in vacuo, the product (5.1 g, 96.1% pure by GLC) was recrystallized from hexane (15 ml).

Alkaline Peroxide Oxidation

Hydrogen peroxide (5 ml, 28%) was added in five portions during 5 min to a solution of methyl 9(10)-formylstearate (5 g) in ethanol (20 ml) containing potassium hydroxide (5 g). After the exothermic reaction subsided the solution was refluxed for 2 hr, poured into water and acidified. The product was extracted with ether, washed with water till neutral and then stripped to dryness. The crystalline product (4.8 g) analyzed as the methyl esters by GLC contained 5.1% oleate + stearate, 31.2% 9(10)-ketostearate, 32.2% methyl 9(10)-hydroxystearate and 27.4% methyl carboxystearate. Two recrystallizations of the product from hexane (15 ml) gave a mixture of keto- and hydroxystearic acids. The mixed product was esterified with diazomethane and the esters (in hexane) were passed through alumina (25 g). The ketostearate eluted with hexane was recrystallized from methanol and identified by IR and GLC. The alumina column was eluted with methanol to give methyl hydroxystearate (crystallized from hexane) identified by IR and GLC analysis.

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